

Formation of noble gas compounds with alkali oxides and sulfides under pressure

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The cubic antiferroite structure comprises a face-centered cubic sublattice of anions with cations on the tetrahedral sites. The voids in the antiferroite structure that are crucial for superionicity in Li_2O might also act as atomic traps. Trapping of guest atoms and small molecules within voids of a host structure leads to the formation of what are known as clathrate compounds. Here we investigate the possibility of trapping helium or larger neon guest atoms under pressure within alkali metal oxide and sulfide structures and find stable helium and neon bearing compounds even at pressures below 1 GPa. These structures are stabilized by a reduction in volume from incorporation of helium or neon atoms within the antiferroite structure. Our study suggests a novel class of alkali oxide and sulfide materials incorporating noble gas atoms that might potentially be useful for gas storage.

Alkali metal oxides are used in catalysing reactions [1], capture and storage of CO_2 [2], gas detectors, and for lowering the work function of photo-cathodes [3]. Lithium oxide (Li_2O) is a key battery material, and it is also used within the nuclear industry. At low pressures alkali oxides [4–13] and sulfides [14–19] normally crystallize in the antiferroite structure of space group $Fm\bar{3}m$, which contains octahedral voids, see Fig. 1. Li_2O exhibits superionic conductivity at temperatures above 1200 K in which diffusing Li^+ ions carry electrical current by hopping from one void to another, while the oxygen atoms remain within a rigid framework [20, 21]. These voids in the antiferroite structure that are crucial for superionicity in Li_2O might also act as atomic traps. Trapping of guest atoms and small molecules within voids of a host structure can lead to the formation of what are known as clathrate compounds [22]. Clathrates involving many different guest species have been observed, such as clathrate hydrates with inclusion of helium (He) [23] or neon (Ne) [24] atoms, or other noble gas atoms. Noble gas compounds have been reviewed by Grochala [25].

Here we investigate the possibility of trapping He or larger Ne guest atoms under pressure within alkali metal oxide and sulfide structures. By studying different noble gas atoms, alkali oxides and sulfides, we are able to study the effects of changing both the host and guest species. At zero pressure there is no thermodynamic driving force for including He or Ne atoms within the alkali oxides or sulfides. The inertness of He and Ne suggests that they might be included within structures containing voids without substantial changes in the host structure. Structures containing voids are unlikely to be stable at high pressures, and it is more likely that the thermodynamically stable state at high pressures of, say, a mixture of He and Li_2O , will consist of hexagonal-close-packed (hcp) He and a dense high-pressure phase of Li_2O . The energetic stability of structures consisting of He or Ne atoms trapped in the antiferroite structures of alkali ox-

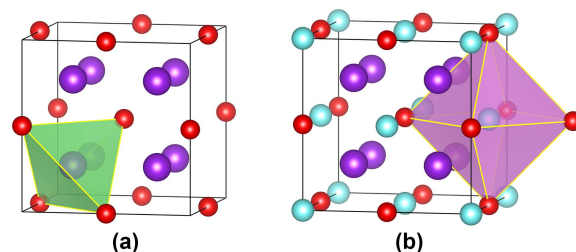


FIG. 1. Crystal structure of antiferroite alkali metal oxide with and without helium atoms. (a) The antiferroite structure of Na_2O . The Na atoms are shown in purple and oxygen atoms in red. The Na atoms occupy tetrahedral positions, and one of the Na atoms is shown at the center of its green tetrahedron. (b) He atoms (light blue) are included within the octahedral voids, and one of the octahedrons is highlighted in purple with a He atom visible at its center.

ides and sulfides therefore rests on a delicate balance of competing effects.

The ambient and high pressure structures of alkali metal sulfides have been studied extensively, and good agreement between experiment and the results of first-principles density-functional-theory (DFT) calculations has been found [8]. There is also good agreement between experiment and DFT results for alkali metal oxides under ambient conditions, although their high-pressure behavior has not been studied in depth experimentally, except for Li_2O [7, 9].

A transition from the antiferroite to orthorhombic anticotunnite structure of $Pnma$ symmetry has been observed in Li_2O at pressures around 50 GPa [7, 9]. Transitions from the antiferroite to anticotunnite structures have also been reported in Li_2S at 12 GPa [15], Na_2S at 7 GPa [16] and in Rb_2S below 0.7 GPa [18]. Interestingly, the anticotunnite structure has not been observed in K_2S , and a distorted Ni_2In -type structure of space

group $P6_3/mmc$ has instead been found at 6 GPa [17]. A transition from the antifluorite structure has been observed in Rb_2S below 0.7 GPa, followed by a transition to a Ni_2In -type structure at 2.6 GPa [18]. Cs_2S has been reported to crystallize in the anticotunnite structure [14] under ambient conditions, and to transform into a distorted Ni_2In -type structure by about 5 GPa [19].

We have performed calculations using the CASTEP plane-wave DFT code [26] to investigate the possibility of the inclusion of He and Ne atoms within alkali oxides and sulfides. Default CASTEP ultrasoft pseudopotentials [27] and a plane-wave basis set energy cutoff of 800 eV were used. We employed the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) density functional [28]. The Brillouin zone was sampled using a k -point grid of spacing $2\pi \times 0.1 \text{ \AA}^{-1}$ for the searches, and a finer spacing of $2\pi \times 0.03 \text{ \AA}^{-1}$ for the final converged results reported in this paper.

We used the *ab initio* random structure searching (AIRSS) method to find structures of alkali oxides and sulfides containing He or Ne atoms. In the AIRSS approach randomly chosen structures are relaxed to minima in the enthalpy [29, 30]. AIRSS has been successfully applied to many systems, including alkali metals, [31], and various oxides such as carbon monoxide [32]. We performed AIRSS calculations for a variety of Na/O/He stoichiometries at a pressure of 15 GPa. The most stable Na/O compound at 15 GPa was found to be Na_2O in the antifluorite structure, as expected, and we found the anticotunnite structure and a Ni_2In -type structure of space group $P6_3/mmc$. We also found a structure of chemical composition $HeNa_2O$ in which Na_2O adopts the antifluorite structure and the He atoms sit at the octahedral voids, so that the $Fm\bar{3}m$ symmetry of the antifluorite structure is maintained. The $HeNa_2O$ structure was found to be slightly more stable than antifluorite Na_2O at 15 GPa. We proceeded to investigate the possibility of stable antifluorite structures of alkali oxides and sulfides with He or Ne atoms placed at the octahedral voids. We then widened our study to include other competitive structures of the alkali oxides and sulfides.

As well as the antifluorite and anticotunnite structures, we considered the $CdCl_2$ ($R\bar{3}m$), γUS_2 ($P\bar{6}2m$), and the $CaCl_2$ ($Pnnm$) structures of the oxides, and $Pnnm$, $Pmma$ and $P6_3/mmc$ structures of the alkali metal sulfides. We found that the enthalpy-pressure curves of the $Pmma$ phase reported for K_2S in Ref. 17 were very close to those of the $P6_3/mmc$ structure for the sulfides from Li_2S to Cs_2S at the pressures studied, and therefore we have not reported results for $Pmma$. The energetically competitive structures were relaxed, and their relative enthalpies are reported in Fig. 2. Interestingly, we found that the transition from the antifluorite to anticotunnite structure in Na_2O occurs at fairly low pressures, but at higher pressures a transition back to antifluorite with included He atoms occurs. We also found structures in

which it is energetically favorable for He atoms to enter the antifluorite structure directly under pressure (K_2O , K_2S , Rb_2S and Cs_2S), and for Ne atoms to enter the antifluorite structure directly (K_2S , Rb_2S and Cs_2S). Further details of the phase transition pressures are reported in the Supplemental Material [33].

Consider a static lattice calculation of the total enthalpy $H = U + pV$, where U is the total internal energy, p is the pressure and V is the volume. Taking $Na_2O + He$ as an example, the reduction in the total volume on forming $HeNa_2O(Fm\bar{3}m)$ at 20 GPa corresponds to about 1/4 of the volume of a He atom in hcp He at the same pressure. We find that the formation of $HeNa_2O(Fm\bar{3}m) + hcp He$ from $He + Na_2O(Fm\bar{3}m)$ increases the total internal energy by 129 meV per formula unit, but the pV term decreases by 186 meV per formula unit. This shows that although the interactions between the He atoms and the host antifluorite Na_2O are not energetically favorable, the reduction in volume from inclusion of the He atoms lowers the overall enthalpy. The pressure derivative of the enthalpy is equal to the volume ($dH/dp = V$), so that the slopes of the curves in Fig. 2 give the volumes relative to the reference $HeNa_2O(Fm\bar{3}m)$ phase (denoted by the dashed-dotted line). The most stable form at low pressures is $Na_2O(Fm\bar{3}m) + hcp He$, which transforms into $Na_2O(Pnma) + hcp He$ at 11.5 GPa. At 14.5 GPa a transformation occurs to $HeNa_2O(Fm\bar{3}m)$, which is stable up to just above 100 GPa. We observe from the slopes of the enthalpy-pressure curves in Fig. 2 that at 14.5 GPa the volume of $HeNa_2O(Fm\bar{3}m)$ is smaller than that of the other $Na_2O + He$ phases. The thermodynamic driving force for the initial incorporation of He atoms is therefore the associated reduction in total volume. A maximum in the enthalpy reduction from He inclusion in Na_2O occurs at about 40 GPa. At higher pressures the stability of the inclusion compound is reduced because the voids in the compressed antifluorite structure are no longer large enough to accommodate the He atoms, which results in an increase in the internal energy, and $HeNa_2O(Fm\bar{3}m)$ eventually becomes unstable to formation of the $P6_3/mmc$ structure just above 100 GPa, see Fig. 2.

The transition pressures for noble gas inclusion are lower for the sulfides than the oxides because the larger size of the S atom leads to larger octahedral voids in the sulfide structures. There is an upper pressure limit to the stability of each of the noble gas compounds discussed here, which depends on the sizes and chemical identities of the host and guest species. The larger stabilization enthalpies of Ne atoms in alkali sulfides compared with He is due to the better matching of the size of the Ne atom with that of the voids in the antifluorite sulfide structures. More pV energy is gained by including a Ne atom within the antifluorite structure rather than a smaller He atom. If the void is large enough the additional strain energy from including the larger Ne atom is small, and

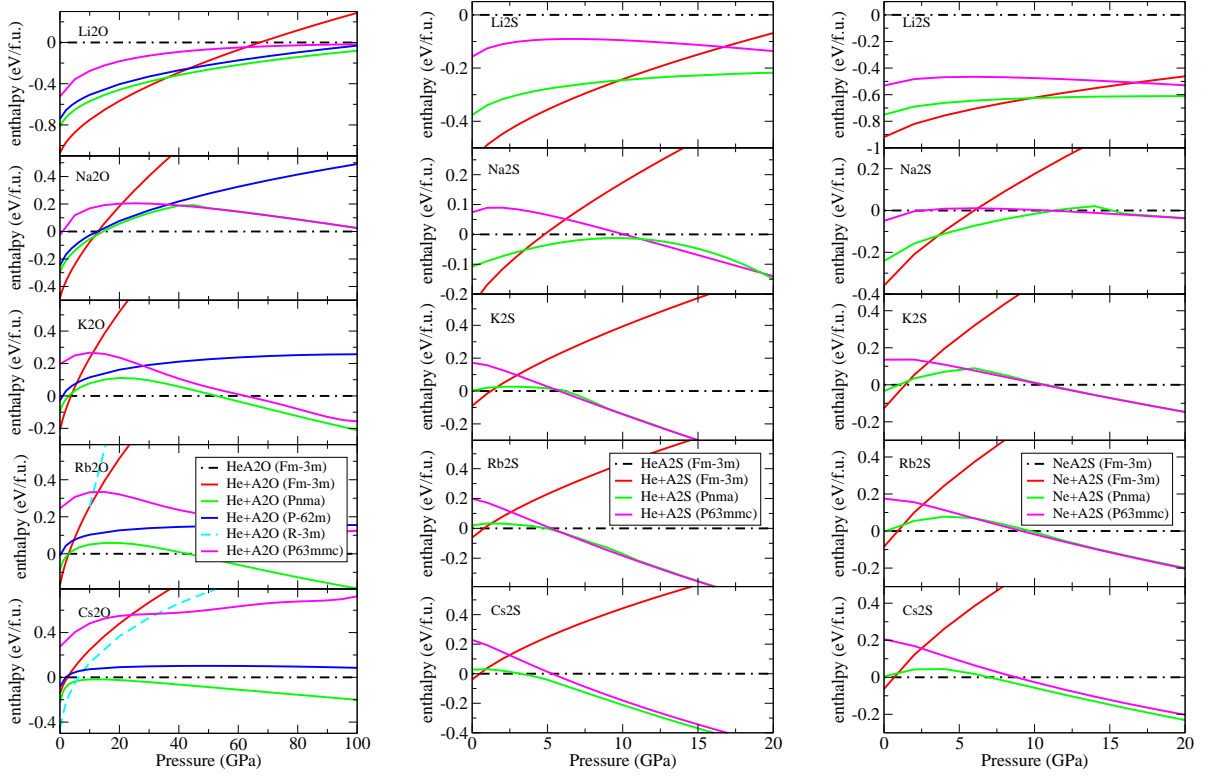


FIG. 2. Enthalpy-pressure relations for the noble gas compounds. (a) He in alkali metal oxides, (b) He in alkali metal sulfides, and (c) Ne in alkali metal sulfides. The enthalpies are given with respect to those of the alkali oxides/sulfides with included noble gas atoms.

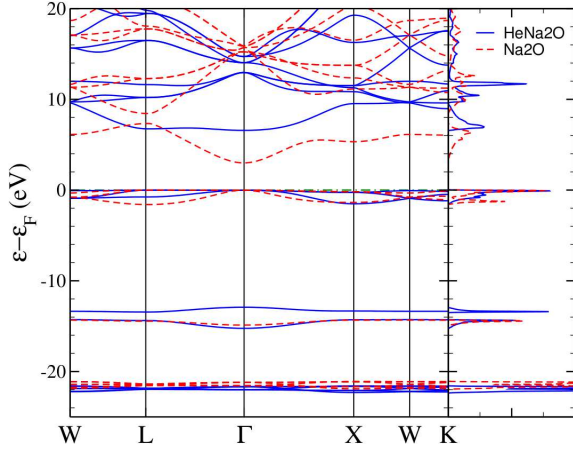


FIG. 3. Electronic Band structures and Density of states of Na_2O (red dashed line) and HeNa_2O (blue solid line) at 20 GPa. The zero of energy is at the valence band maximum. The He 1s band lies at about -13.5 eV.

it is energetically favorable to include the Ne atom. In other words, the stabilization enthalpy is largest at pressures for which the sizes of the voids and included alkali atoms are well matched.

We find ranges of stability for antifluorite HeK_2O and HeRb_2O , as well as HeNa_2O , but HeLi_2O and HeCs_2O

are thermodynamically unstable at the pressures studied, see Fig. 2. The stability ranges are 14.5–105 GPa (HeNa_2O), 3.7–53 GPa (HeK_2O), and 3.0–43 GPa (HeRb_2O). Replacing the O atoms by larger S atoms we find that HeLi_2S and HeNa_2S are not stable, but that HeK_2S , HeRb_2S , and HeCs_2S have small regions of stability at low pressures with small stabilization enthalpies. The stability ranges are 1.3–5.8 GPa (HeK_2S), 0.8–4.9 GPa (HeRb_2S), and 0.5–4.9 GPa (HeCs_2S), see Fig. 2. The inclusion of He atoms within the alkali sulfides is therefore not particularly favorable. Replacing the He atoms by larger Ne atoms, we find that stable neon alkali sulfides in the antifluorite structure occur for NeK_2S , NeRb_2S , and NeCs_2S , but not for NeLi_2S and NeNa_2S . The stability ranges are also larger: 1.4–10.6 GPa (NeK_2S), 0.9–9.2 GPa (NeRb_2S), and 0.7–7.0 GPa (NeCs_2S), see Fig. 2. The maximum stabilization energies for the helium alkali oxides, helium alkali sulfides, and neon alkali sulfides are: 188 meV (HeNa_2O at 41 GPa); 33 meV (HeRb_2S at 1.4 GPa); and 78 meV (NeK_2S at 5.5 GPa).

Each of the materials investigated is an insulator. The bandstructures of the alkali oxides and sulfides consist of narrow and rather widely spaced bands, as shown in Fig. 3 for Na_2O at a pressure of 20 GPa. The orbitals at the valence band maximum arise mainly from the O $2p$

levels, which capture the valence $3s$ electrons from the Na atoms. The bands at about -14.5 eV arise from the O $2s$ levels, and those at -22.0 eV arise from the Na $2p$ levels. When He atoms are added they occupy a band at about -13.5 eV which shows a small amount of hybridization with the O $2s$ levels. The Na $2s$ levels lie at about -50 eV (not shown).

In K_2S at 2 GPa the O $2p$ levels capture the K $4s$ electrons, and the O $2s$ levels lie at about -9.4 eV. The K $3p$ levels lie at about -12.6 eV. When He atoms are included they occupy a $1s$ band which is very close in energy to the K $3p$ levels, and there is considerable hybridization between these orbitals, see the Supplemental Material [33]. If Ne atoms are included instead of He, we find that the Ne $2p$ levels sit at an energy of about -10.0 eV, just below the O $2s$ levels.

The inclusion of noble gas atoms does not in general alter the oxygen, sulfur or alkali-metal-derived bands very much, which is consistent with the interaction between the noble gas atoms and the host oxide/sulfide being fairly weak. However, in some cases significant hybridization between the alkali atom and O $2s$ levels can occur. Bandstructures for other oxides and sulfides, with and without included He and Ne atoms are shown in the Supplemental Material [33].

Inclusion of He or Ne atoms within the alkali oxides and sulfides increases their band gaps. For example, at 2 GPa the band gap of K_2S is increased by about 0.4 eV on inclusion of Ne atoms, and by 1.2 eV for He atoms. The band gap of Na_2O at 20 GPa is increased by 1.1 eV on including Ne atoms, but by 3.5 eV for He atoms. In the cases that we have studied, the band gaps are increased more by including He atoms than Ne atoms. We have investigated the origin of the increased band gaps by performing calculations for the oxides and sulfides at the larger volumes of the compounds that include noble gas atoms. We find that the increased gaps are mainly due to the presence of the noble gas atoms, rather than the increase in volume. This arises because the electronic states at the conduction band minimum have a significant weight within the voids of the antifluorite structure, and the presence of the noble gas atoms pushes these states to higher energies. The band gaps that we have obtained with the PBE functional are a factor of about two smaller than experimental values for Li_2O (8 eV [34]), Na_2O (4.4-5.8 eV [35]), and K_2O (4.0-5.4 eV [35]). Results from quasiparticle bandstructure calculations within the G_0W_0 approximation [36] agree quite well with the available experimental data. Underestimation of band gaps within standard DFT calculations is well-known, but the changes in band gaps due to the introduction of the noble gas atoms are likely to be significantly more accurate than the gaps themselves.

The phonon bandstructures of K_2S and NeK_2S at 5 GPa shown in Fig. 4 indicate that the Ne atoms give rise to Einstein-oscillator-like bands at about 110 cm^{-1} . We

have investigated the dynamical stability of the $Fm\bar{3}m$ structures with incorporated noble gas atoms, finding that HeK_2S and $HeNa_2O$ are stable down to zero pressure, and therefore they might be quench recoverable under ambient conditions. HeK_2S is, however, dynamically unstable at low pressures, but it is stabilized by pressures of a few GPa, see Figs. 6 and 7 of the Supplemental Material [33]. At the static lattice level and a pressure of 5 GPa, NeK_2S is about 80 meV/fu more stable than $Ne+K_2S$, but when quasi-harmonic phonon enthalpies are added the stability of NeK_2S is reduced to 54 meV/fu. Similarly, at the static lattice level and a pressure of 40 GPa, $HeNa_2O$ is about 187 meV/fu more stable than $He+Na_2O$. Including vibrational zero-point energy reduces this to 175 meV/fu. We have found strong evidence that materials such as $HeNa_2O$ and NeK_2S could be thermodynamically stable under pressure, and that it might be possible to synthesize them. More information about the phonon bandstructures is provided in the Supplemental Material [33].

The inclusion of noble gas atoms might be detected via an increase in lattice constant observable in x-ray diffraction, or in Raman or infrared (IR) vibrational spectroscopy. The antifluorite oxides and sulfides, without noble gas atoms, have one Raman and one IR active vibrational mode. Inclusion of Ne atoms in K_2S at 5 GPa leads to the appearance of an additional vibrational mode at around 110 cm^{-1} , as can be seen in Fig. 4. The zone-center mode of NeK_2S at around 110 cm^{-1} is IR active, and the NeK_2S/K_2S modes around 150 cm^{-1} are Raman active, and those around 230 cm^{-1} are IR active. The calculated Raman and IR intensities for NeK_2S/K_2S at 5 GPa are shown in the Supplemental Material [33]. The appearance of a new IR active vibrational mode of NeK_2S at around 110 cm^{-1} , the shifts in the Raman and IR frequencies, and the changes in Raman intensity could be used as signatures of the inclusion of Ne atoms. Similar data for the inclusion of He within Na_2O at 40 GPa are reported in the Supplemental Material [33]. As condensed He or Ne are commonly used as the pressure transmission medium in diamond-anvil-cell experiments [37], our results are also relevant to the question of whether these atoms could enter alkali oxides and sulfides in diamond-anvil-cell experiments.

In summary, we have predicted the stability of compounds at high pressures in which He or Ne atoms are included within alkali metal oxides or sulfides. In some cases structures including noble gas atoms are predicted to become thermodynamically stable at pressures below 1 GPa. The chemical interactions between the host oxide or sulfide and the guest noble gas atoms is weak, and the materials discussed here may be described as inclusion compounds. Our study suggests a new class of metal/noble gas inclusion compounds that could be synthesized under applied pressure, and might be useful for gas storage. It seems likely that many more compounds

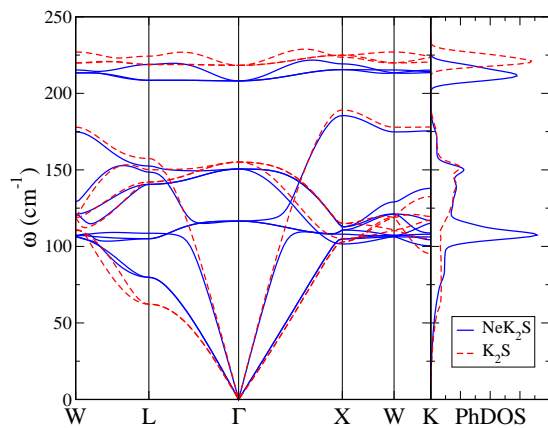


FIG. 4. Phonon bandstructures and density of states of K_2S (red dashed line) and NeK_2S (blue solid line) at 5 GPa. The Ne-derived vibrations give Einstein-oscillator-like phonon bands at about 110 cm^{-1} , which show some hybridization with the K_2S -derived bands.

containing noble gas atoms could be stabilized by pressure.

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